



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 934 959 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
11.08.1999 Bulletin 1999/32

(51) Int Cl⁶: C08F 283/12, C08G 77/46

(21) Application number: 99300807.7

(22) Date of filing: 03.02.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 06.02.1998 US 19578 *Feb 6 1998*

(71) Applicant: DOW CORNING CORPORATION
Midland Michigan 48686-0994 (US)

(72) Inventors:
• Meinhardt, David Randall
Midland, Michigan 48642 (US)
• Zhang, Shizhong
Midland, Michigan 48640 (US)

(74) Representative: Kyle, Diana
Elkington and Fife
Prospect House
8 Pembroke Road
Sevenoaks, Kent TN13 1XR (GB)

(54) Method of making (meth)acrylate polyether grafted and crosslinked silicone elastomers

(57) Silicone elastomers are made by crosslinking reactions of =Si-H containing siloxanes and an unsaturated hydrocarbon such as an alpha, omega-diene, in the presence of a low molecular weight siloxane fluid. The =SiH siloxane is first partially reacted with either a monoacrylate functionalized polyether or a monomethacrylate functionalized polyether. It is then crosslinked by the alpha, omega-diene in the presence of the low molecular weight siloxane fluid. An elastomer, i.e. gel,

with polyether groups is produced. The elastomer gel can be swollen with the low molecular weight siloxane fluid under shear force to provide a uniform silicone paste. The silicone paste has excellent spreadability upon rubbing and possesses unique rheological properties in being thixotropic and shear thinning. The silicone paste is easily emulsified with water to form a stable uniform emulsion without using a surfactant to allow normally immiscible materials to become intimately mixed.

EP 0 934 959 A1

Description

[0001] This invention is directed to the thickening of low molecular weight siloxane fluids or solvents. More particularly, the siloxane fluids or solvents are swollen by a silicone elastomer, i.e., a silicone gel.

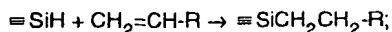
5 [0002] The swollen silicone elastomer gel can be used in that form or it can be converted into a silicone paste or a silicone emulsion, if desired.

[0003] Cross-links are junctions of polymer strands in a three-dimensional network. They may be viewed as long-chain branches which are so numerous that a continuous insoluble network or gel is formed.

10 [0004] Platinum catalyzed hydrosilylation reactions have been used to form networks. Typically, such reactions involve a low molecular weight siloxane containing $\equiv\text{Si}-\text{H}$ groups and a high molecular weight siloxane containing $\equiv\text{Si}-\text{vinyl}$ groups or vice versa.

[0005] Attractive features of this mechanism are that (i) no by-products are formed, (ii) cross-linking sites and hence network architecture can be narrowly defined, and (iii) hydrosilylation will proceed even at room temperature to form the networks. In the mechanism, crosslinking involves addition of $\equiv\text{SiH}$ across double bonds, i.e.,

15



or crosslinking involves addition of $\equiv\text{SiH}$ across triple bonds, i.e.,

20



25 [0006] We have utilized this mechanism, but by employing some unobvious and unique modifications of the mechanism, we have been able to formulate a new range of product forms having new and unique properties and ranges of application.

[0007] In particular, one unique aspect is that our silicone paste can be used to form an emulsion without the need of a surfactant. This is of considerable value in the personal care arena where skin sensitivity due to the presence of certain surfactants is an issue.

30 [0008] Our invention relates to a method of making a silicone elastomer by a first step of reacting (A) a $\equiv\text{Si}-\text{H}$ containing polysiloxane; and (B) either a monoacrylate functionalized polyether or a monomethacrylate functionalized polyether; in the presence of a platinum catalyst, until an $\equiv\text{Si}-\text{H}$ containing siloxane with polyether groups is formed, i.e., a polysiloxane containing polyether substituents and residual silicon hydride groups. In a second step according to our method, we react (C) the polysiloxane containing polyether substituents and residual silicon hydride groups; and (D) an unsaturated hydrocarbon such as an alpha, omega-diene; in the presence of (E) a solvent and a platinum catalyst, until a silicone elastomer is formed by crosslinking and addition of $\equiv\text{SiH}$ across double bonds in the alpha, omega-diene.

35 [0009] Our invention is not limited to swelling silicone elastomers with only low molecular weight polysiloxanes. Other types of solvents can swell the silicone elastomer. Thus, a single solvent or a mixture of solvents may be used.

40 [0010] By solvent we mean (i) organic compounds, (ii) compounds containing a silicon atom, (iii) mixtures of organic compounds, (iv) mixtures of compounds containing a silicon atom, or (v) mixtures of organic compounds and compounds containing a silicon atom; used on an industrial scale to dissolve, suspend or change the physical properties of other materials.

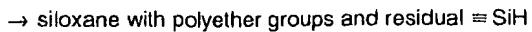
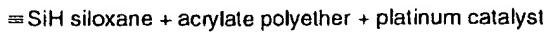
45 [0011] As another feature of our invention, additional solvent is added to the silicone elastomer while the solvent and silicone elastomer are sheared until a silicone paste is formed.

[0012] As a further feature of our invention, water is added to the silicone paste and the water and silicone paste are sheared until a silicone emulsion is formed. The silicone emulsion is formed free of the presence of a surfactant.

50 [0013] Silicone elastomers, silicone pastes and silicone emulsions, prepared according to these methods, have particular value and utility in treating hair, skin or underarm areas of the human body. In addition, the silicone elastomers, silicone pastes and silicone emulsions, are capable of forming barrier films after evaporation of any solvent or volatile component.

Step 1: Incorporation of the polyether

55



Step 2: Gelation

siloxane with polyether groups and residual $\equiv\text{SiH}$ + $\equiv\text{SiH}$

5 siloxane (optional) + alpha, omega-diene + low molecular weight siloxane fluid + platinum catalyst \rightarrow gel (elastomer)

10 Step 3: Shearing and swelling

gel (elastomer) + siloxane fluid + shear \rightarrow paste

15 Step 4: Emulsification

silicone paste + water + shear \rightarrow silicone emulsion

20 [0014] In Step 1, the molar ratio of the polyether to the $\equiv\text{SiH}$ in the siloxane is in the range of 0.01 to less than 1.0.
 20[0015] In Step 2, the weight ratio of the low molecular weight siloxane fluid to the weight of the $\equiv\text{SiH}$ siloxane with
 25 other groups and the alpha, omega-diene is from 1-98, but preferably is between 3-10. The molar ratio of the $\equiv\text{SiH}$
 25groups in the siloxane with polyether groups to unsaturated groups in the alpha, omega-diene is from 20:1 to 1:20, but
 must include a polyether group.

[0016] For example, one formulation found especially suitable for Step 2 is a mixture containing the following com-
 pounds:



1,5-hexadiene and decamethylcyclopentasiloxane.

[0017] In the above formulas and hereinafter, Me represents the group $-\text{CH}_3$ and Q represents the group $-\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})(\text{OCH}_2\text{CH}_2)_9\text{OCH}_3$.

[0018] In Step 3, the silicone paste contains 80-98 percent by weight of the low molecular weight siloxane fluid or other fluid or solvent to be thickened.

[0019] In Step 4, the weight ratio of water to the silicone paste is from 95:5 to 5:95.

[0020] The $\equiv\text{Si-H}$ containing polysiloxane is represented by compounds of the formula $\text{R}_3\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}''\text{HSiO})_b\text{SiR}_3$ referred to as type A¹ and compounds of the formula $\text{HR}_2\text{SiO}(\text{R}'_2\text{SiO})_c\text{SiR}_2\text{H}$ or compounds of the formula $\text{HR}'_2\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}''\text{HSiO})_b\text{SiR}_2\text{H}$ referred to as type A². In the three formulas, R, R' and R'', are alkyl groups with 1-6 carbon atoms; a is 0-250; b is 1-250; and c is 0-250. The molar ratio of compounds A²:A¹ is 0-20, preferably 0-5. In preferred embodiments, compounds of types A¹ and A² are used in the reaction; however, it is possible to successfully conduct the reaction using only compounds of type A¹. If desired, these $\equiv\text{Si-H}$ containing polysiloxanes can also include trifunctional T units $\text{RSiO}_{3/2}$ and tetrafunctional Q units $\text{SiO}_{4/2}$.

[0021] The $\equiv\text{Si-H}$ containing polysiloxane A¹ also comprises an alkylhydrogen cyclosiloxane or an alkylhydrogen-dialkyl cyclosiloxane copolymer, represented in general by the formula $(\text{R}'_2\text{SiO})_d(\text{R}''\text{HSiO})_e$ where R' and R'' are as defined above, d is 0-10 and e is 3-10. Some representative compounds are $(\text{OSiMeH})_4$, $(\text{OSiMeH})_3(\text{OSiMeC}_6\text{H}_{13})$, $(\text{OSiMeH})_2(\text{OSiMeC}_6\text{H}_{13})_2$ and $(\text{OSiMeH})(\text{OSiMeC}_6\text{H}_{13})_3$, where Me represents $-\text{CH}_3$. If desired, these $\equiv\text{Si-H}$ containing polysiloxanes can also include trifunctional T units $\text{RSiO}_{3/2}$ and tetrafunctional Q units $\text{SiO}_{4/2}$.

[0022] The most preferred unsaturated hydrocarbon is an alpha, omega-diene of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_x\text{CH}=\text{CH}_2$ where x is 1-20. Some representative examples of suitable alpha, omega-dienes for use herein are 1,4-pentadiene; 1,5-hexadiene; 1,6-heptadiene; 1,7-octadiene; 1,8-nonadiene; 1,9-decadiene; 1,11-dodecadiene;

1,13-tetradecadiene and 1,19-eicosadiene.

[0023] However, other unsaturated hydrocarbons are useful such as alpha, omega-diyne of the formula $\text{CH} \equiv \text{C}(\text{CH}_2)_x\text{C} \equiv \text{CH}$; or alpha, omega-ene-yne of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_x\text{C} \equiv \text{CH}$ where x is 1-20. Some representative examples of suitable alpha, omega-diyne for use herein are 1,3-butadiyne $\text{HC} \equiv \text{C}-\text{C} \equiv \text{CH}$ and 1,5-hexadiyne (dipropargyl) $\text{HC} \equiv \text{C}-\text{CH}_2\text{CH}_2-\text{C} \equiv \text{CH}$. One representative example of a suitable alpha, omega-ene-yne for use herein is hexene-5-yne-1 $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{C} \equiv \text{CH}$.

[0024] In addition, our invention contemplates the use of other types of unsaturated materials such as siloxane monomers or siloxane polymers containing two or more terminal alkenyl groups; two or more pendant alkenyl groups; or two or more terminal and pendant groups. One suitable siloxane, for example, is 1,3-divinyltetramethyldisiloxane $\text{H}_2\text{C}=\text{CH}(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2\text{CH}=\text{CH}_2$. Representative of further siloxanes which can be employed are vinyl terminated polydimethylsiloxanes containing more than two silicon atoms; vinyl terminated diphenylsiloxane-dimethylsiloxane copolymers; vinyl terminated polyphenylmethylsiloxanes; vinyl terminated trifluoropropylmethylsiloxane-dimethylsiloxane copolymers; vinyl terminated diethylsiloxane-dimethylsiloxane copolymers; trimethylsiloxy terminated vinylmethylsiloxane-dimethylsiloxane copolymers; vinyl terminated vinylmethylsiloxane-dimethylsiloxane copolymers; and vinylmethylsiloxane homopolymers.

[0025] The reactions in Steps 1 and 2 require a catalyst to effect the reaction between the $\equiv \text{SiH}$ containing siloxanes, the monoacrylate/monomethacrylate functionalized polyether and the alpha, omega-diene. Suitable catalysts are Group VII transition metals, i.e., the noble metals. Such noble metal catalysts are more fully described in US Patent 3,923,705 to show typical platinum catalysts. One preferred platinum catalyst is Karstedt's catalyst, which is described in Karstedt's US Patents 3,715,334 and 3,814,730. Karstedt's catalyst is a platinum divinyl tetramethyl disiloxane complex, typically containing about one weight percent of platinum or less, carried in a polydimethylsiloxane fluid or in a solvent such as toluene.

[0026] The particular catalyst used in our examples was Karstedt's catalyst as a 0.5 weight percent of platinum carried in a two centistoke (mm^2/s) polydimethylsiloxane fluid. Another preferred platinum catalyst is a reaction product of chloroplatinic acid and an organosilicon compound containing terminal aliphatic unsaturation. It is described in US Patent 3,419,593. The noble metal catalysts are used in amounts from 0.00001-0.5 part per 100 weight parts of $\equiv \text{SiH}$ containing polysiloxane, preferably 0.00001-0.02 part, most preferably 0.00001-0.002 part.

[0027] The monoacrylate functionalized polyether used herein is a compound of the formula $\text{CH}_2=\text{CHCOO}[\text{CH}_2\text{CH}_2\text{O}]_m[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_n[\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{O}]_p\text{T}$. The monomethacrylate functionalized polyether used herein is a compound of the formula

$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}[\text{CH}_2\text{CH}_2\text{O}]_m[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_n[\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{O}]_p\text{T}$. In these formulas, T represents an end group which is hydrogen atom; a C_1 - C_{30} linear or branched chain alkyl group such as methyl, ethyl, propyl, butyl, decyl and octadecyl; an aryl group such as phenyl; or a C_1 - C_{20} acyl group such as acetyl, propionyl, butyryl, lauroyl, myristoyl and stearoyl. m, n and p, each represent integers which are equal to zero or have values of 1-100. Most preferably, however, m, n and p, are not equal to zero. Such monoacrylate functionalized polyethers and monomethacrylate functionalized polyethers are commercially available from companies such as the Sartomer Company of West Chester, Pennsylvania under the trademark SARTOMER®.

[0028] In a case where m, n and p are all equal to zero and T is a long alkyl group such as C_{18} , for example, the resulting silicone elastomeric product is rendered more hydrophobic, with the result that the silicone paste is more compatible with aliphatic materials such as hydrocarbon waxes and mineral oil.

[0029] The phrase low molecular weight siloxane fluid is intended to include (i) low molecular weight linear and cyclic volatile methyl siloxanes, (ii) low molecular weight linear and cyclic volatile and non-volatile alkyl and aryl siloxanes, and (iii) low molecular weight linear and cyclic functional siloxanes. Most preferred, however, are low molecular weight linear and cyclic volatile methyl siloxanes (VMS).

[0030] VMS compounds correspond to the average unit formula $(\text{CH}_3)_a\text{SiO}_{(4-a)/2}$ in which a has an average value of two to three. The compounds contain siloxane units joined by $\equiv \text{Si-O-Si} \equiv$ bonds. Representative units are monofunctional "M" units $(\text{CH}_3)_3\text{SiO}_{1/2}$ and difunctional "D" units $(\text{CH}_3)_2\text{SiO}_{2/2}$.

[0031] The presence of trifunctional "T" units $\text{CH}_3\text{SiO}_{3/2}$ results in the formation of branched linear or cyclic volatile methyl siloxanes. The presence of tetrafunctional "Q" units $\text{SiO}_{4/2}$ results in the formation of branched linear or cyclic volatile methyl siloxanes.

[0032] Linear VMS have the formula $(\text{CH}_3)_3\text{SiO}((\text{CH}_3)_2\text{SiO})_y\text{Si}(\text{CH}_3)_3$. The value of y is 0-5. Cyclic VMS have the formula $((\text{CH}_3)_2\text{SiO})_z$. The value of z is 3-6. Preferably, these volatile methyl siloxane have a boiling point less than 250°C. and a viscosity of 0.65-5.0 centistoke (mm^2/s).

[0033] Representative linear volatile methyl siloxanes are hexamethyldisiloxane (MM) with a boiling point of 100°C., viscosity of 0.65 mm^2/s and formula $\text{Me}_3\text{SiOSiMe}_3$; octamethyltrisiloxane (MDM) with a boiling point of 152°C., viscosity of 1.04 mm^2/s and formula $\text{Me}_3\text{SiOMe}_2\text{SiOSiMe}_3$; decamethyltetrasiloxane (MD₂M) with a boiling point of 194°C., viscosity of 1.53 mm^2/s and formula $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_2\text{SiMe}_3$; dodecamethylpentasiloxane (MD₃M) with a boiling point of 229°C., viscosity of 2.06 mm^2/s and formula $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_3\text{SiMe}_3$; tetradecamethylhexasiloxane (MD₄M) with a

boiling point of 245°C., viscosity of 2.63 mm²/s and formula $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_4\text{SiMe}_3$; and hexadecamethylheptasiloxane (MD_6M) with a boiling point of 270°C., viscosity of 3.24 mm²/s and formula $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_5\text{SiMe}_3$.

[0034] Representative cyclic volatile methyl siloxanes are hexamethylcyclotrisiloxane (D_3) a solid with a boiling point of 134°C. and formula $\{(\text{Me}_2\text{SiO})_3\}$;

5 octamethylcyclotetrasiloxane (D_4) with a boiling point of 176°C., viscosity of 2.3 mm²/s and formula $\{(\text{Me}_2\text{SiO})_4\}$; decamethylcyclopentasiloxane (D_5) with a boiling point of 210°C., viscosity of 3.87 mm²/s and formula $\{(\text{Me}_2\text{SiO})_5\}$; and dodecamethylcyclohexasiloxane (D_6) with a boiling point of 245°C., viscosity of 6.62 mm²/s and formula $\{(\text{Me}_2\text{SiO})_6\}$.

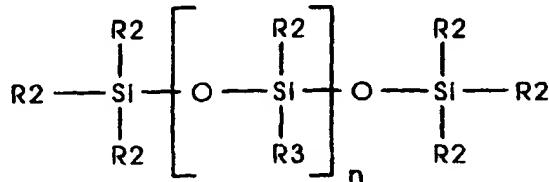
10 [0035] Representative branched volatile methyl siloxanes are heptamethyl-3-((trimethylsilyl)oxy)trisiloxane ($M_3\text{T}$) with a boiling point of 192°C., viscosity of 1.57 mm²/s and formula $\text{C}_{10}\text{H}_{30}\text{O}_3\text{Si}_4$; hexamethyl-3,3,bis ((trimethylsilyl)oxy) trisiloxane ($M_4\text{Q}$) with a boiling point of 222°C., viscosity of 2.86 mm²/s and formula $\text{C}_{12}\text{H}_{36}\text{O}_4\text{Si}_5$; and pentamethyl-((trimethylsilyl)oxy) cyclotrisiloxane (MD_3) with the formula $\text{C}_8\text{H}_{24}\text{O}_4\text{Si}_4$.

15 [0036] Our process can include the use of low molecular weight linear and cyclic volatile and non-volatile alkyl and aryl siloxanes. Representative linear polysiloxanes are compounds of the formula $\text{R}_3\text{SiO}(\text{R}_2\text{SiO})_y\text{SiR}_3$ and representative cyclic polysiloxanes are compounds of the formula $(\text{R}_2\text{SiO})_z$. R is an alkyl group of 1-6 carbon atoms or an aryl group such as phenyl. The value of y is 0-80, preferably 0-20. The value of z is 0-9, preferably 4-6. These polysiloxanes have a viscosity generally in the range of 1-100 centistoke (mm²/s).

[0037] Other representative low molecular weight non-volatile polysiloxanes have the general structure:

20

25



where n has a value to provide polymers with a viscosity in the range of 100-1,000 centistoke (mm²/sec).

30 [0038] R2 and R3 are alkyl radicals of 1-20 carbon atoms or an aryl group such as phenyl. Typically, the value of n is 80-375. Illustrative polysiloxanes are polydimethylsiloxane, polydiethylsiloxane, polymethylethylsiloxane, polymethylphenylsiloxane and polydiphenylsiloxane.

35 [0039] Low molecular weight functional polysiloxanes are generally represented by acrylamide functional siloxane fluids, acrylate functional siloxane fluids, amide functional siloxane fluids, amino functional siloxane fluids, carbinol functional siloxane fluids, carboxy functional siloxane fluids, chloroalkyl functional siloxane fluids, epoxy functional siloxane fluids, glycol functional siloxane fluids, ketal functional siloxane fluids, mercapto functional siloxane fluids, methyl ester functional siloxane fluids, perfluoro functional siloxane fluids and silanol functional siloxanes.

40 [0040] In general, the organic compounds are aromatic hydrocarbons, aliphatic hydrocarbons, alcohols, aldehydes, ketones, amines, esters, ethers, glycals, glycol ethers, alkyl halides or aromatic halides. Representative of some common organic solvents are alcohols such as methanol, ethanol, 1-propanol, cyclohexanol, benzyl alcohol, 2-octanol, ethylene glycol, propylene glycol and glycerol; aliphatic hydrocarbons such as pentane, cyclohexane, heptane, Varnish Makers and Painters (VM&P) naphtha and mineral spirits; alkyl halides such as chloroform, carbon tetrachloride, perchloroethylene, ethyl chloride and chlorobenzene; amines such as isopropylamine, cyclohexylamine, ethanolamine and diethanolamine; aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene; esters such as ethyl acetate, isopropyl acetate, ethyl acetoacetate, amyl acetate, isobutyl isobutyrate and benzyl acetate; ethers such as ethyl ether, n-butyl ether, tetrahydrofuran and 1,4-dioxane; glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monobutyl ether and propylene glycol monophenyl ether; ketones such as acetone, methyl ethyl ketone, cyclohexanone, diacetone alcohol, methyl amyl ketone and diisobutyl ketone; petroleum hydrocarbons such as mineral oil, gasoline, naphtha, kerosene, gas oil, heavy oil and crude oil; lubricating oils such as spindle oil and turbine oil; and fatty oils such as corn oil, soybean oil, olive oil, rape seed oil, cotton seed oil, sardine oil, herring oil and whale oil.

45 [0041] "Other" miscellaneous organic solvents can be used, such as acetonitrile, nitromethane, dimethylformamide, propylene oxide, trioctyl phosphate, butyrolactone, fufural, pine oil, turpentine and m-creosol.

50 [0042] We further intend to encompass by the term solvent, volatile flavoring agents such as oil of wintergreen; peppermint oil; spearmint oil; menthol; vanilla; cinnamon oil; clove oil; bay oil; anise oil; eucalyptus oil; thyme oil; cedar leaf oil; oil of nutmeg; oil of sage; cassia oil; cocoa; licorice; high fructose corn syrup; citrus oils such as lemon, orange, lime and grapefruit; fruit essences such as apple, pear, peach, grape, strawberry, raspberry, cherry, plum, pineapple and apricot; and other useful flavoring agents including aldehydes and esters such as cinnamyl acetate, cinnamalde-

hyde, eugenyl formate, p-methylanisole, acetaldehyde, benzaldehyde, anisic aldehyde, citral, nerol, decanal, vanillin, tolyl aldehyde, 2,6-dimethyloctanal and 2-ethyl butyraldehyde.

[0043] In addition, we intend the term solvent to include volatile fragrances such as natural products and perfume oils. Some representative natural products and perfume oils are ambergris, benzoin, civet, clove, leaf oil, jasmine, mate', mimosa, musk, myrrh, orris, sandalwood oil and vetivert oil; aroma chemicals such as amyl salicylate, amyl cinnamic aldehyde, benzyl acetate, citronellol, coumarin, geraniol, isobornyl acetate, ambrette and terpinyl acetate; and the various classic family perfume oils such as the floral bouquet family, the oriental family, the chypre family, the woody family, the citrus family, the canoe family, the leather family, the spice family and the herbal family.

[0044] Our process is carried out stepwise by combining the =SiH containing siloxane(s), the monoacrylate functionalized polyether or the monomethacrylate functionalized polyether, the alpha, omega-diene, the low molecular weight siloxane or solvent and the platinum catalyst; and mixing these ingredients at room temperature until a gel, elastomer, paste or emulsion is formed. If desired, the gel, elastomer, paste or emulsion can be further diluted with an additional similar or dissimilar solvent(s), to form the final composition. A blend of hexane and tetrahydrofuran, a fragrance, an oil or another low molecular weight siloxane, are examples of diluents that could be so employed. Higher temperatures to speed up the process can further be used.

[0045] Additional amounts of low molecular weight siloxane or solvent can be added to the gel, i.e., Step 3, while the resulting mixture is subjected to shear force to form the paste. In Step 4, shear force is again used, during or after water is added to the paste to form the emulsion. Any type of mixing and shearing equipment may be used to perform these steps such as a batch mixer, planetary mixer, single or multiple screw extruder, dynamic or static mixer, colloid mill, homogenizer, sonicator or a combination thereof.

[0046] Typically, we carry out the process using approximately a 1:1 molar ratio of the =Si-H containing siloxane with polyether groups and the alpha, omega-diene. It is expected that useful materials may also be prepared by carrying out the process with an excess of either the =Si-H containing siloxane or the alpha, omega-diene but this would be considered a less efficient use of the materials. The remainder of the composition comprises the low molecular weight siloxane or solvent, in amounts generally within the range of 65-98 percent by weight of the composition, but preferably 80-98 percent by weight.

[0047] The silicone elastomer, silicone gel and silicone paste compositions of our invention have particular value in the personal care arena. Because of the unique volatility characteristics of the VMS component of these compositions, they can be used alone or blended with other cosmetic fluids, to form a variety of over-the-counter (OTC) personal care products.

[0048] Thus, they are useful as carriers in antiperspirants and deodorants, since they leave a dry feel and do not cool the skin upon evaporation. They are lubricious and will improve the properties of skin creams, skin care lotions, moisturizers, facial treatments such as acne or wrinkle removers, personal and facial cleansers, bath oils, perfumes, colognes, sachets, sunscreens, pre-shave and after-shave lotions, liquid soaps, shaving soaps and shaving lathers. They can be used in hair shampoos, hair conditioners, hair sprays, mousses, permanents, depilatories and cuticle coats, to enhance gloss and drying time and provide conditioning benefits.

[0049] In cosmetics, they will function as leveling and spreading agents for pigments in make-ups, color cosmetics, foundations, blushes, lipsticks, lip balms, eyeliners, mascaras, oil removers, color cosmetic removers and powders. They are useful as delivery systems for oil and water soluble substances such as vitamins. When incorporated into sticks, gels, lotions, aerosols and roll-ons, the compositions impart a dry, silky-smooth, payout.

[0050] In addition, the compositions exhibit a variety of advantageous and beneficial properties such as clarity, shelf stability and ease of preparation. Hence, they have wide application, but especially in antiperspirants, deodorants, in perfumes as a carrier and for conditioning hair.

[0051] Our silicone elastomers, gels and pastes have uses beyond the personal care arena, including their use as a filler or insulation material for electrical cable, a soil or water barrier or as a replacement for epoxy materials used in the electronics industry.

[0052] They are also useful as carrier for crosslinked silicone rubber particles. In that application, (i) they allow ease of incorporation of the particles into such silicone or organic phases as sealants, paints, coatings, greases, adhesives, antifoams and potting compounds; and (ii) they provide for modifying rheological, physical or energy absorbing properties of such phases in either their neat or finished condition.

[0053] In addition, our silicone elastomers, gels and pastes are capable of functioning as carriers for pharmaceuticals, biocides, herbicides, pesticides and other biologically active substances; and can be used to incorporate water and water-soluble substances into hydrophobic systems. Examples of some water-soluble substances are salicylic acid, glycerol, enzymes and glycolic acid.

[0054] Our invention, therefore, provides another viable route to the production of a stable uniform emulsion without employing a surfactant, allowing normally immiscible materials to become intimately mixed, by using a monoacrylate functionalized polyether or a monomethacrylate functionalized polyether. As noted above, this can be of considerable value in the personal care arena where skin sensitivity due to the presence of certain surfactants can be an issue.

[0055] The following examples are set forth for the purpose of illustrating our invention in more detail.

Example 1

5 [0056] 50 gram of an organopolysiloxane with the average structure $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{93} (\text{MeHSiO})_6\text{SiMe}_3$ where Me is $-\text{CH}_3$, 2.98 gram of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2\text{CH}_2\text{O})_9\text{CH}_3$ a compound sold under the trademark Sartomer® CD-550 by the Sartomer Company of West Chester, Pennsylvania and 231.40 gram of decamethylcyclopentasiloxane (D_5) were mixed and heated to 100 °C. and then 0.577 gram of Karstedt's catalyst containing 0.5 weight percent platinum was added. After 20 minutes, 15.606 gram of a mixture containing 10% by weight of 1,5-hexadiene
10 $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ and 90% by weight of decamethylcyclopentasiloxane was added to the solution. Gelation occurred within one hour. The gel was heated in an oven at 70°C. for two hours. Then one part by weight of the gel was swollen with one part by weight of decamethylcyclopentasiloxane under shear force. The resulting uniform paste had a viscosity of 90,000 cP (mPa·s). The paste was mixed with deionized water in a 5:1 weight ratio in a glass jar using a mechanical stirrer. A smooth opaque white emulsion formed having a viscosity of 126,000 cP (mPa·s). Viscosity
15 was measured using a Brookfield DV-II Viscometer having a TC-type spindle operating at 2.5 rpm (0.26 rad/s).

Example 2

20 [0057] 50 gram of an organopolysiloxane having the average structure $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{93} (\text{MeHSiO})_6\text{SiMe}_3$, 2.98 gram of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2\text{CH}_2\text{O})_9\text{CH}_3$, i.e., Sartomer® CD-550 and 298.09 gram of decamethylcyclopentasiloxane were mixed and heated to 100°C. and then 0.701 gram of Karstedt's catalyst containing 0.5 weight percent of platinum was added. After 20 minutes, 13.259 gram of a silicone polymer having the average structure $(\text{Vi})\text{Me}_2\text{SiO}(\text{SiMe}_2\text{O})_6\text{SiMe}_2(\text{Vi})$ where Vi is $\text{H}_2\text{C}=\text{CH}-$ was added. Gelation occurred within one hour. The gel was heated in an oven at 70°C. for two hours. Then one part by weight of the gel was swollen with one part by weight of decamethylcyclopentasiloxane under shear force. The resulting uniform paste had a viscosity of 63,000 cP (mPa·s). The paste was mixed with deionized water in a 5:1 weight ratio in a glass jar using a mechanical stirrer. A smooth opaque white emulsion was formed having a viscosity of 78,000 cP (mPa·s).

Example 3 - Comparative

30 [0058] 50 gram of the copolymer $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{93}(\text{MeHSiO})_6\text{SiMe}_3$ used in Examples 1 and 2 and 229.92 gram of decamethylcyclopentasiloxane were mixed and heated to 70°C. Then 0.583 gram of Karstedt's catalyst containing 0.5 weight percent of platinum and 17.835 gram of a mixture containing 10% by weight of 1,5-hexadiene and 90% by weight of decamethylcyclopentasiloxane was added to the solution. Gelation occurred within a few minutes. The gel was heated in an oven at 70°C. for 3 hours. Then seven parts by weight of the gel was swollen with five parts by weight of decamethylcyclopentasiloxane under shear force. The resulting uniform paste had a viscosity of 100,000 cP (mPa·s). The paste was mixed with deionized water in a 5:1 weight ratio in a glass jar using a mechanical stirrer. In this example, however, water could not be dispersed.

40

Claims

1. A method of making a silicone elastomer comprising as a first step, reacting:

45 (A) an $\equiv\text{Si-H}$ containing polysiloxane of the formula $\text{R}_3\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}''\text{HSiO})_b\text{SiR}_3$ or the formula $(\text{R}'_2\text{SiO})_d$ ($\text{R}''\text{HSiO})_e$ and, optionally, an $\equiv\text{Si-H}$ containing polysiloxane of the formula $\text{HR}_2\text{SiO}(\text{R}'_2\text{SiO})_c\text{SiR}_2\text{H}$ or an $\equiv\text{Si-H}$ containing polysiloxane of the formula $\text{HR}_2\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}''\text{HSiO})_b\text{SiR}_2\text{H}$, where R, R' and R'' are alkyl groups with 1-6 carbon atoms, a is 0-250, b is 1-250, c is 0-250, d is 0-10 and e is 3-10; and
50 (B) a monoacrylate functionalized polyether of the formula $\text{CH}_2=\text{CHCOO}[\text{CH}_2\text{CH}_2\text{O}]_m[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_n[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_p\text{T}$ or a monomethacrylate functionalized polyether of the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}[\text{CH}_2\text{CH}_2\text{O}]_m[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_n[\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{O}]_p\text{T}$, where T represents hydrogen; a C₁-C₃₀ linear or branched chain alkyl group, an aryl group or a C₁-C₂₀ acyl group; and m, n and p, each represent integers which are either equal to zero or have values of 1-100; in the presence of a platinum catalyst, until a polysiloxane is formed containing polyether substituents and residual silicon hydride groups; and as a second step, reacting components comprising:
55 (C) the polysiloxane containing polyether substituents and residual silicon hydride groups;
(D) an unsaturated hydrocarbon selected from the group consisting of alpha, omega-dienes of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_x\text{CH}=\text{CH}_2$, alpha, omega-diyne of the formula $\text{CH}\equiv\text{C}(\text{CH}_2)_x\text{C}\equiv\text{CH}$ and alpha, omega-ene-

yne of the formula $\text{CH}_2=\text{CH}(\text{CH}_2)_x\text{C}\equiv\text{CH}$, where x is 1-20 or an unsaturated siloxane monomer or siloxane polymer containing two or more terminal alkenyl groups; two or more pendant alkenyl groups; or two or more terminal and pendant groups; in the presence of

(E) a solvent selected from the group consisting of (i) organic compounds, (ii) compounds containing a silicon atom, (iii) mixtures of organic compounds, (iv) mixtures of compounds containing a silicon atom, and (v) mixtures of organic compounds and compounds containing a silicon atom; and in the presence of a platinum catalyst, until a silicone elastomer is formed by crosslinking and addition of $\equiv\text{SiH}$ across double or triple bonds in the unsaturated hydrocarbon.

- 10 2. A method according to claim 1 in which the second step includes as an additional reactant (F) an $\equiv\text{Si-H}$ containing polysiloxane of the formula $\text{R}_3\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}''\text{HSiO})_b\text{SiR}_3$ or the formula $(\text{R}'_2\text{SiO})_d(\text{R}''\text{HSiO})_e$ and, optionally, an $\equiv\text{Si-H}$ containing polysiloxane of the formula $\text{HR}_2\text{SiO}(\text{R}'_2\text{SiO})_c\text{SiR}_2\text{H}$ or an $\equiv\text{Si-H}$ containing polysiloxane of the formula $\text{HR}_2\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}''\text{HSiO})_b\text{SiR}_2\text{H}$, where R, R' and R'' are alkyl groups with 1-6 carbon atoms, a is 0-250, b is 1-250, c is 0-250, d is 0-10 and e is 3-10.
- 15 3. A method according to claims 1 or 2 including the further step of adding additional amounts of solvent(s) to the silicone elastomer while shearing the solvent(s) and silicone elastomer until a silicone paste is formed.
- 20 4. A method according to claim 3 including the further steps of adding water to the silicone paste and shearing the water and silicone paste until a silicone emulsion is formed.
5. A method according to claim 4 wherein the silicone emulsion is prepared without addition of a surfactant.
- 25 6. A method according to any of claims 1 to 5, in which the solvent is a linear volatile methyl siloxane of the formula $(\text{CH}_3)_3\text{SiO}((\text{CH}_3)_2\text{SiO})_y\text{Si}(\text{CH}_3)_3$ where y is 0-5 or a cyclic volatile methyl siloxane of the formula $\{(\text{CH}_3)_2\text{SiO}\}_z$ where z is 3-8 and the volatile methyl siloxane has a boiling point less than 250°C. and a viscosity of 0.65-5.0 centistokes (mm^2/s).
- 30 7. A method according to any of claims 1 to 6, in which the molar ratio of the monoacrylate functionalized polyether and the monomethacrylate functionalized polyether to the silicon hydride groups in the $\equiv\text{SiH}$ containing polysiloxane is in the range of 0.01 to less than 1.0; m, n and p, are not all equal to zero; and the $\equiv\text{Si-H}$ containing polysiloxane optionally includes trifunctional T units $\text{RSiO}_{3/2}$ and tetrafunctional Q units $\text{SiO}_{4/2}$.
- 35 8. A method according to any of claims 1 to 7, in which the second step, the weight ratio of the solvent to the weight of the polysiloxane containing polyether substituents and residual silicon hydride groups and the unsaturated hydrocarbon is 1-98.
9. A method according to any of claims 1 to 8, in which the second step, the molar ratio of the polysiloxane containing polyether substituents and residual silicon hydride groups and the unsaturated hydrocarbon is 20:1 to 1:20.
- 40 10. A personal care product comprising a silicone elastomer prepared by the method of claim 1 or 2, or a silicone paste prepared by the method of claim 5 or a silicone emulsion prepared by the method of claim 4 or 5.
11. A method of providing a barrier film to the surface of a substrate comprising applying to said substrate a silicone elastomer prepared by the method of claim 1 or 2 or a silicone paste prepared by the method of claim 5 or a silicone emulsion prepared by the method of claim 4 or 5.

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 99 30 0807

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 298 402 A (DOW CORNING) 11 January 1989 * page 8, line 35 - line 54 * * claims *	1-11	C08F283/12 C08G77/46
A	US 5 412 004 A (TACHIBANA KIYOMI ET AL) 2 May 1995 * page 7, column 12, line 15 - line 36 * * example 1 *	1-11	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08F C08G
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	4 May 1999	Pollio, M	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 0807

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

04-05-1999

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 0298402	A	11-01-1989		US 4853474 A		01-08-1989
				DE 3874825 A		29-10-1992
				JP 1030633 A		01-02-1989
				JP 2653676 B		17-09-1997
US 5412004	A	02-05-1995		JP 5140320 A		08-06-1993
				JP 6040847 A		15-02-1994
				JP 6040848 A		15-02-1994
				EP 0545002 A		09-06-1993